Improved density-functional calculations for molecules and calculation of adsorption of the heaviest elements on surfaces

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In 1964 Hohenberg and Kohn [1] were able to show that the total energy of any system in an external field can be described by a functional of its density only. This pioneer work is the basis of the Density Functional Theory (DFT) and provides an incentive for many theoreticians to find this functional. In the last three decades many approximations for the energy density functional were made which gave quite good results, but the 'exact' form of the functional is still unknown.

DFT calculations depend on the choice of the exchange-correlation functional and the treatment of the kinetic energy. The spectrum of the different approximations of the kinetic energy starts with a purely non-relativistic approach with or without spin-orbit interaction, continues with the Zeroth-Order Regular Approximation (ZORA) [2, 3] and ends with a full-relativistic description. A comparison of these approximations and corresponding results can be found in [4, 5].

An important difference between various density functionals is the treatment of the spin of the electrons. In the simplest form of non-relativistic density functionals spin is completely neglected. This approximation works quite well for closed-shell systems but leads to wrong results for open-shell molecular as well as atomic systems. A very important improvement was achieved by extending these functionals to spin-polarized (SP) forms [6]. In a relativistic description the spin should actually be included in the relativistic form of the density functionals, which directly depend on the four current density, but this approach is not yet suitable for practical applications. Alternatively, the spin can be included into the relativistic form of the density functionals in a theoretically consistent way via the magnetization density using a fictitious external magnetic field which is set to zero in the end formulas (for more details see [7, 8]).

In this case the exchange and/or correlation functionals depend not only on the density but also on the magnetization density (see details in [7, 8, 9]). The magnetization density at any point in space is defined as magnetic moment per volume [10]. Following this, it is a vector which, in general, points to different directions at different points in space. In order to simplify the calculations in most implementations the magnetization density is aligned to the axis of the highest symmetry (z-axis), which in the literature is called the collinear approximation. There are only few implementations of the non-collinear approximations for atoms and solids known in the literature [9, 11, 12]. Only one of them reports an implementation for molecules where the authors used a scalar-relativistic description [13]. In a recent letter [14] we were able to present the first four-component implementation of the non-collinear density functionals for the diatomic molecule Pt_2. The accuracy which is achieved with this method is better than 0.2 eV in contrast to the old type of calculations without the inclusion of the magnetization density.

In the context of the very first molecular calculations which include transactinide elements with this new method we present results for $RfCl_4$ and its homologues. Again the difference between the theoretical and the experimental results of $ZrCl_4$ and $HfCl_4$ indicate a maximal error of 0.2 eV. This gives us hope that this method can be used as calculational tool with chemical relevant accuracy.

A second improvement for future calculations of very heavy systems will be demonstrated in the adsorption of single atoms on surfaces. In order to detect a very heavy element atom like e.g.112 thermographic chromatography is a method which often is used. The physical quantity which determines the adsorption of the single atom on a surface is the binding energy. For this element 112 we present our first results where the surface is either determined by a cluster or alternatively by an embedding procedure which simulates the surface. Comparison with the homologue Hg leads to a good prediction of the adsorption energy of element 112.

References

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